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(54) Cylindrical alkaline battery

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CLAIM

A type of cylindrical alkaline battery characterized by the following facts: the cylindrical alkaline battery has a cylindrical metal case that contains a positive electrode, a negative electrode, and a cylindrical separator with bottom; on this cylindrical metal case, a ring-shaped groove portion that bends inward is formed; on this groove portion, a sealing plate, which also acts as the negative electrode terminal, in combination with a sealing ring that is L-shaped in cross section, which has at least a portion of the surface covered with a sealant, is carried to seal

the battery; in this battery, the portion of the cylindrical separator positioned on the inner side of said ring-shaped groove portion and in contact with the ring-shaped groove portion is covered with an alkali-resistant cylindrical insulating film.

DETAILED EXPLANATION OF THE INVENTION

In recent years, the cylindrical batteries originating with manganese dry batteries have been gradually replaced by the crystal alkaline batteries using alkaline electrolyte as they have excellent properties, such as high voltage stability, good low-temperature characteristics, high-rate characteristics, high capacity, etc. However, as for the caustic alkali used as the electrolyte, as it can creep up on the metal surface significantly, leakage may take place easily, and prevention of the leakage becomes a major topic to be addressed. Recently, however, with popularization of computers and other electronic equipment, the current consumption becomes lower, and there is a high demand on development of batteries with high capacity and good shelf storage property over a long time. Consequently, it has become a technical topic to develop a type of cylindrical alkaline battery that has little increase in voltage and capacity at least over 2-3 years, and can maintain a high resistance to leakage.

According to this invention, the battery makes use of manganese dioxide (MnO_2), silver oxide (AgO), mercury oxide (HgO), etc. as the negative electrode active substance, zinc as negative electrode active substance, and caustic alkali as electrolyte. In this battery, on a cylindrical metal case that also acts as the positive electrode terminal, a ring-shaped groove portion that bends inward is formed. The purpose of this invention is to prevent decrease in the voltage during storage of the cylindrical alkaline battery. For this purpose, the portion of the cylindrical separator positioned on the inner side of said ring-shaped groove portion and in contact with the ring-shaped groove portion is covered with an alkali-resistant cylindrical insulating film. In this way, direct contact between the separator and the ring-shaped groove portion is prevented; it is possible to prevent decrease in the voltage during storage.

Figure 1 is a diagram illustrating the typical structure of the cylindrical alkaline battery having the ring-shaped groove portion. In Figure 1, (1) represents a sealing plate made of a 3-layer clad plate composed of nickel (Ni), stainless steel and copper (Cu). The peripheral portion is formed by bending in the direction almost perpendicular to the radial direction of the sealing plate to a U-shaped cross section. This sealing plate also acts as the negative electrode terminal. On the surface of copper on the inner side of the sealing plate, collector (2) is spot-welded. The material of the collector may be copper or brass, which allows easy amalgamation, as well as iron sheet plated with tin (Sn). (3) represents sealing ring with L-shaped cross section which is combined with sealing plate (1) in a liquid tight state. It may be made of nylon 6.6, nylon 11,

polyethylene, polypropylene, or other thermoplastic resin. The surface of the portion in contact with the portion with U-shaped cross section of the peripheral edge of the sealing plate is coated with pitch, asphalt, chlorosulfonated polyethylene, polyamide resin, polybutene, or other sealing agent so as to maintain the tight sealing state with the sealing plate. (4) represents the cylindrical positive electrode case that also acts as the positive electrode terminal. It has ring-shaped groove portion (4a) that bends inward near the opening portion. On this ring-shaped groove portion, sealing ring (3) in combination with sealing plate (1), and the upper end of the case is curled inward to perform sealing. In order to improve the sealing property between the sealing ring and the positive electrode case, on the surface of the positive electrode case in contact with the sealing ring, a sealant is coated just as in the case of the sealing ring. The material of the case may be prepared by plating nickel (Ni) or gold (Au) with a thickness of 3-6 μm on a cold rolled steel sheet. (5) represents a positive electrode composite. It is a cylindrical molding of a mixture of manganese dioxide, silver oxide, mercury oxide, or other active substance and a powder of flake-shaped graphite, acetylene black, or other electroconductive substance. (6) represents a cylindrical separator with bottom. Its outer periphery is in contact with the positive electrode composite, and its upper end is in contact with sealing plate (4), with its interior filled with negative electrode composite (7). Negative electrode composite (7) is prepared from a blend of amalgamated zinc powder, potassium hydroxide (KOH) as the electrolyte, polyacrylic acid sodium, carboxymethyl cellulose, etc. (8) represents a heat-shrunk tube made of polyvinyl chloride. It acts as the package. For the cylindrical battery with said constitution, the most important role is played by the ring-shaped groove portion. Many measures have been taken against the leakage that would otherwise take place easily as potassium hydroxide used as electrolyte in the alkaline battery has a significant ability in creeping up the metal surface due to the electrocapillary phenomenon. In the method in which a sealing plate is carried on the ring-shaped groove portion for sealing, the ring-shaped groove portion is needed to keep the sealing plate in a stable state without deformation under the pressure applied in the sealing operation when the battery with high resistance to leakage is formed. For this purpose, it is important to have the groove formed with bending towards the inner side of the positive electrode case as deep as possible. If the groove is shallow, the sealing plate cannot be carried on it well, and the sealing plate is partially submerged under the pressure applied for sealing, or a gap may be developed between the coupled sealing plate and sealing ring, leading to significant degradation in the leak resistance. Consequently, as shown in Figure 1, the ring-shaped groove portion is bent until the position where it is in contact with the separator. However, as the ring-shaped groove portion is formed by bending and stretching a portion of the positive electrode case inward. As the surface of nickel or gold plating layer cannot follow well the stretching of the feed material, fine cracks are formed. The iron as the feed material bulges out through the small

cracks. For the battery in this state, during the storage, zinc of the negative electrode slowly penetrates through the separator. When the grown zinc reaches the ring-shaped groove portion, internal short circuit takes place. The self-consumption of the active substance starts decrease in the voltage. This degradation in the voltage takes place particularly early when the battery is stored at a high temperature, and this has a major adverse influence on the performance of the battery. For the aforementioned conventional structure with the ring-shaped groove portion, although the structure has a good leak resistance, voltage degradation takes place during storage. This is a major disadvantage.

According to this invention, the aforementioned problem is solved by covering the portion of the cylindrical separator on the inner side of the ring-shaped groove portion and in contact with the ring-shaped groove portion with an alkali-resistant cylindrical insulating film. In the following, the contents of this invention will be explained. Figure 2 is an enlarged cross-sectional view of the sealing portion. In this figure, (1) represents the sealing plate; (3) represents the sealing ring; (4) represents the positive electrode case; (5) represents the positive electrode composite; (6) represents the separator; (7) represents the negative electrode composite; (8) represents a package; (9) represents an alkali-resistant cylindrical insulating film. In the structure of the battery, after cylindrical positive electrode composite (8) is inserted into positive electrode case (4), ring-shaped groove portion (4a) is formed. Then, cylindrical separator with bottom (6) is inserted into cylindrical positive electrode composite (5). Cylindrical insulating film (9) having a diameter larger than the outer diameter of separator (6) and smaller than the inner diameter of the ring-shaped groove portion is inserted to the outer side of separator (6). In addition, after electrolyte is loaded beforehand in separator (6), negative electrode composite (7) made of a blend of zinc, electrolyte, and a thickener is filled. Then, collector-attached sealing plate (1) in combination with sealing ring (3) is carried on ring-shaped groove portion (4a) to seal the battery. Examples of the materials that can be used to form alkali-resistant cylindrical insulating film (9) include polytrifluoroethylene, polytetrafluoroethylene, polyethylene, nylon 6, polypropylene, polyester, polyvinyl chloride, polyvinylidene chloride, polystyrene, ionomer, and other polymer films. The thickness should be at least 10 μm so that no pinhole is formed. When the insulating film is inserted on the outer side of the separator, several methods may be adopted, such as the method in which the overlap portion of the film shown in Figure 2 is bonded by heat or adhesive, the method in which insertion is made in the state when the overlap portion of the film is not fixed. Any of these methods may be adopted. Also, the inserting position may be such that the lower portion of cylindrical film (9) reaches the positive electrode composite surface, and it is not in contact with the positive electrode composite. It is important that adjustment is performed such that cylindrical film (9) is

positioned in the portion where ring-shaped groove portion (4a) and separator (6) are in contact or nearest to each other.

By covering an alkali-resistant cylindrical insulating film on the outer side of the cylindrical separator in contact with the ring-shaped groove portion, there is no direct contact between the surface of the ring-shaped groove portion where iron is exposed and the separator. Consequently, even when the battery is stored, zinc from the negative electrode does not penetrate through the separator to reach the ring-shaped groove portion, so that it is possible to prevent voltage degradation due to self-consumption of the active substance. The following table lists the number of cases of voltage degradation among the 100 cylindrical mercury batteries of the prior art and 100 cylindrical mercury batteries of this invention.

N=100

Batteries	Storage period (days)						
	0	20	40	60	80	100	120
Prior art	0	0	0	3	12	27	48
This invention	0	0	0	0	0	0	0

It can be seen that for the conventional batteries, the voltage degrade significantly after about 60 days. After 120 days, about 60% of the batteries degraded. On the other hand, for the batteries of this invention, there is no degradation in voltage after 120 days. That is, the effect is significant. In this way, this invention has a characteristic feature that it is free of the disadvantage of the prior art of degradation in voltage due to self-consumption of the active substance during storage. The storage property of the battery is improved significantly. That is, this invention can provide a type of battery with much better storage property.

BRIEF DESCRIPTION OF FIGURES

Figure 1 is a cross-sectional view illustrating the structure of a typical cylindrical alkaline battery. Figure 2 is an oblique view of the alkali-resistant cylindrical insulating film used in an application example of this invention.

1 Sealing plate
2 Collector
3 Sealing ring
4 Positive electrode plate case
4a Ring-shaped groove portion
5 Positive electrode composite

6 Separator

7 Negative electrode composite

9 Alkali-resistant cylindrical insulating film

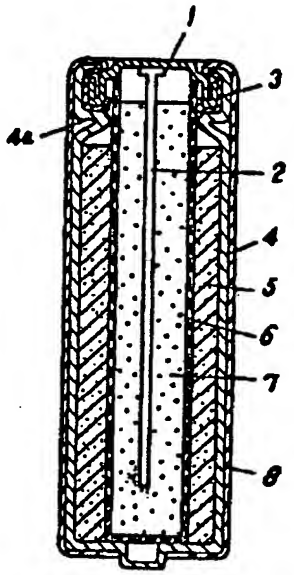

Figure 1

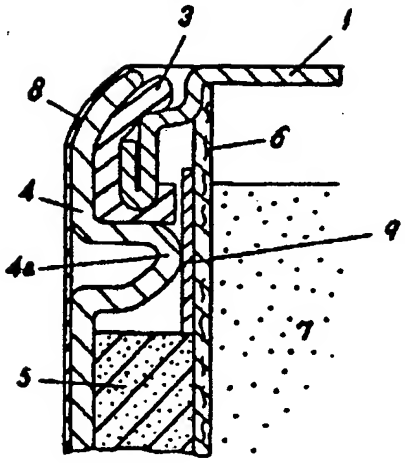

Figure 2

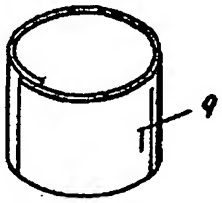

Figure 3

PHOENIX
TRANSLATIONS

...the height of Excellence...

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